ARCADIS

Appendix **B**

Sulfolane Degradation Bench Testing Summary

Technical Memorandum

To: Loren Garner

From: Todd DeJournett

Subject: North Pole Refinery – Summary of Sulfolane Remediation Knowledge

Date: March 20, 2012

Project: 02011001.22

c: Brian Angerman, Brian Sillanpaa, Gary Remple

This memo summarizes the current available knowledge regarding sulfolane remediation mechanisms for the North Pole Refinery site. The available knowledge consists of:

- Published literature
- Results of bench and pilot treatability testing associated with the selection/design of point-of-entry treatment technology for removing sulfolane from drinking water wells.
- Full-scale operational data collected from point-of-entry (POE) treatment system pilots
- Operational data collected from the onsite groundwater remediation system
- Bench testing data collected in conjunction with the onsite remediation system

The purpose of this memo is to synthesize this available knowledge and to identify fundamental mechanisms that may be employed to remediate sulfolane at the site. This document is in support of the broader feasibility studies that will be completed for the onsite and offsite sulfolane impacts.

Knowledge from Published Literature

Natural Attenuation Mechanisms

The majority of the published information regarding the environmental fate of sulfolane suggests that oxidation by aerobic microorganisms is the primary degradation pathway for sulfolane. This view appears to be related to the fact that aerobic sulfolane degradation has been observed by all researchers who studied it, while anaerobic sulfolane degradation has been sporadically observed as further described below.

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Saint-Fort (2006) observed aerobic sulfolane degradation in aquifer microcosms, but no anaerobic degradation. Notably, the reported elemental composition for the sediments used in this study indicated undetectable concentrations of manganese.

Kim et al. (1999) observed anaerobic sulfolane degradation in aquifer microcosms, but did not speculate regarding the mechanism.

Greene et al. (1998) observed anaerobic sulfolane degradation associated with nitrate reduction and manganese reduction in some of their replicates. Notably, manganese oxide was added to some of these replicates to stimulate manganese reduction. Additionally, anaerobic sulfolane degradation was observed in the replicates incubated at 8 degrees C, but not in replicates incubated at 28 degrees C. A significant lag period was observed prior to the onset of manganese reduction and sulfolane degradation. Finally, Greene et al. noted that the amount of reduced manganese observed in the microcosms was insufficient to account for complete mineralization of the sulfolane that disappeared from the microcosms.

The rate of observed sulfolane degradation was reported to have zero-order kinetics in both aerobic and anaerobic sediment microcosms (Greene et al., 1998; Greene and Fedorak, 2001, Saint-Fort, 2006). Additionally, amendment of sediment microcosms with phosphorus, while stimulating the growth of purported sulfolane-degrading organisms, was actually associated with longer lag times and, ultimately, slower sulfolane degradation rates relative to the unamended control (Greene and Fedorak, 2001).

Anaerobic sulfolane degradation resulting in the production of thiolane has been described by some researchers (Kim, 1999), but the general consensus of the literature is that the rates of anaerobic biodegradation of sulfolane are negligible compared to aerobic processes.

Finally, while much of the existing literature regarding environmental fate of sulfolane documents the lack of appearance of stiochiometric amounts of the hypothesized aerobic daughter products (carbon dioxide, sulfuric acid, hydroxybutene sulfonic acid), no other sulfolane degradation metabolites have been documented either.

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Sulfolane in Electrochemistry

A significant body of research exists regarding the utility of sulfolane as an electrolyte in rechargeable batteries. Sulfolane's polarity and low volatility make it an attractive electrolyte for these batteries. Additionally, sulfolane has a tendency to form a passivating film on the surface of the anode, reducing corrosion and enhancing the life of the anode (Watanabe 2008, Lewandowski 2011).

It is noted in the electrochemical literature that sulfolane is resistant to oxidation, but susceptible to reductive attack in these galvanic cells (Kolosnitsyn et al., 2006). This observation is counter to the general observation that oxidative degradation is a more favorable degradation pathway in the environment.

Other researchers have observed dimerization of sulfolane via metal catalysts (Wellisch et al., 1964). The reaction apparently involves the reductive cleavage of the cyclobutene ring, followed by interaction of resulting radicals at the terminal carbon on adjacent butene chains.

Sulfolane Remediation Methods

As summarized in the Sulfolane Technical Assistance and Evaluation Report (Oasis 2010), methods for successfully removing sulfolane from water that have been described in the literature include biological activated carbon (BAC), advanced oxidation using oxidants such as hydrogen peroxide and ozone, sometimes in the presence of ultraviolet light. In general, most of the applications described in the literature were treating water with sulfolane concentrations greater than 1 mg/L.

Sulfolane Deterioration and Regeneration in the Sulfinol Process

As describe in the Sulfolane Technical Assistance and Evaluation Report (Oasis, 2010), sulfolane has a tendency to deteriorate in the sulfinol process loop. This deterioration is thought to be due to intrusion of oxygen into the loop, and is accompanied by an increase in acidity and corrosion of process piping. The degradation products of sulfolane in the sulfinol process loop are not fully known, but are generally thought to be acids or polymers. Other impurities resulting from sulfolane deterioration and corrosion of process piping include iron solids.

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Knowledge from POE Treatability Testing

A feasibility study and report were completed in support of the development of POE treatment systems to remove sulfolane from residential well water (Barr 2011a). As described in the POE Report, a variety of treatment approaches were investigated via bench and pilot testing as part of the technology selection process for POE treatment systems. The approaches studied included:

- Oxidation with potassium permanganate
- Oxidation with hydrogen peroxide
- Oxidation with calcium hypochlorite
- Oxidation with hydrogen peroxide + ultraviolet radiation
- Oxidation with ozone
- Oxidation with ozone + ultraviolet radiation
- Activated carbon adsorption

Activated carbon was found to be more effective than any other methods for removing sulfolane from groundwater. The only advanced oxidation approach that was observed to significantly remove sulfolane from groundwater was ozone + ultraviolet radiation, which achieved a maximum of about 30% removal of sulfolane. Consequently, activated carbon was selected for implementation in the POE treatment systems, as well as the interim onsite remediation system.

Knowledge from Full Scale POE Pilot Testing

As described in the Draft Site Characterization Report (Barr 2011b), data collected from long-term pilot testing of the POE systems suggested carbon life without suflolane breakthrough in excess of expectations based on prior bench and pilot testing. While the reason for the greater than expected treatment capacity of the carbon is unknown, one possible explanation is degradation of adsorbed sulfolane within the carbon bed.

Knowledge from Onsite Remediation System Operation

The onsite remediation system consists of air stripper towers (BTEX removal), a gallery pond, sand filters (to remove solids and prevent fouling of the carbon beds) and four activated carbon adsorbers. As

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described in the Site Draft Site Characterization Report (Barr 2011b) and the quarterly groundwater monitoring reports (Barr 2011b, ARCADIS 2011a, ARCADIS 2011b), the onsite remediation system has exceeded performance expectations based on performance of the POE pilot systems. After processing over 86 million gallons of groundwater, breakthrough of sulfolane still has not been observed in the lead carbon adsorber. While one reason for this greater than anticipated treatment capacity may be degradation within the carbon bed, another reason is the unanticipated low loading of sulfolane to the carbon adsorbers due to loss of sulfolane across the air strippers, gallery ponds, and sand filters. While the degree of removal across these unit processes is variable, it is generally significant, being on the following order:

- Average removal across the air strippers to date based on monitoring data is 21 percent
- Average removal across the gallery pond to date based on monitoring data is 35 percent
- Average removal across the sand filter to date based on monitoring data is 41 percent

The removal of sulfolane across the air strippers, gallery pond, and sand filter does not appear to be impeded by cold temperatures, as high degrees of sulfolane removal are observed in winter and summer alike.

A characteristic aspect of the remediation system is the precipitation of iron/manganese oxides upon aeration in the air stripper. These oxides continue to precipitate in the gallery pond and are filtered out of the water by the sand filters. The sand filter backwash, containing the removed solids, is routed back to the gallery pond, such that iron/manganese solids build up in the gallery pond over time. A generally small fraction of the iron passes through the sand filters and is subsequently removed in the lead activated carbon vessel.

As described in the next section, supplemental bench testing was undertaken to understand the mechanism(s) for sulfolane removal upstream of the activated carbon adsorbers, and to provide information for potential inclusion of the mechanism(s) in the feasibility studies.

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Knowledge from Supplemental Bench Testing

Supplemental bench testing was undertaken to better understand the mechanism(s) responsible for the sulfolane removal observed across the air stripper, gallery pond, and sand filter in the onsite remediation system. This was done through a series of three sets of simple jar tests, progressively more focused around the specific mechanism(s) involved. The objectives for each of the three tests were:

- Test 1 - To identify the aspect of the treatment train responsible for the observed sulfolane removal and formulate an hypothesis regarding the general mechanism(s) involved

- Test 2 - To identify the mechanism(s) involved, understand their likely applicability at in-situ temperatures and oxygen contents, and formulate hypotheses regarding daughter products, intermediates, and limiting factors

- Test 3 - To identify limiting factors, daughter products, and intermediates for the mechanism(s) and refine the conceptual degradation pathway(s) for use in onsite and offsite feasibility studies.

Test 1

Test 1 was conducted onsite in June 2011. This testing consisted of the following treatments, conducted in sealed bottles:

- Photolysis of 0.45-micron filtered air stripper effluent in a fused quartz reactor under ambient sunlight for 2.5 hours. This was compared to an identical dark control.
- Unamended air stripper effluent, incubated at room temperature for 2.5 hours.
- Air stripper effluent with 10 mL/L sand filter backwash, incubated at room temperature for 2.5 hours.
- Air stripper effluent with 100 mL/L sand filter backwash, incubated at room temperature for 2.5 hours.
- Air stripper effluent with 10 mL/L GAC vessel backwash, incubated at room temperature for 2.5 hours.

The results of Test 1 are summarized in Figure 1 below. As shown in Figure 1, neither the 0.45-micron filtered dark control, nor the 0.45-micron filtered photolyzed treatment exhibited significant sulfolane

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removal. In fact, the sulfolane concentrations for these samples were higher than observed for the raw air stripper effluent. In addition to indicating that photolysis was not the likely removal mechanism observed, this finding also suggests that filtration of the samples quenched a sulfolane removal reaction that would otherwise have occurred in the air stripper effluent en route to the laboratory. This phenomenon was not apparent in the air stripper influent, which exhibited the highest sulfolane concentration of all the samples, as expected.

It can be seen that the only treatment to enhance sulfolane removal relative to the unfiltered air stripper effluent was the treatment with 100 mL sand filter backwash solids. The conclusion of Test 1 was therefore that the sulfolane removal mechanism(s) observed were associated with backwash solids and, to a lesser extent, some property of the water that was induced by the air stripper, but removed by filtration. Thus, the hypothesis formulated regarding the removal mechanism(s) was some reaction (biological or abiotic) catalyzed by iron/managanese solids that were formed via oxidation in the air stripper, and concentrated in the sand filter backwash.

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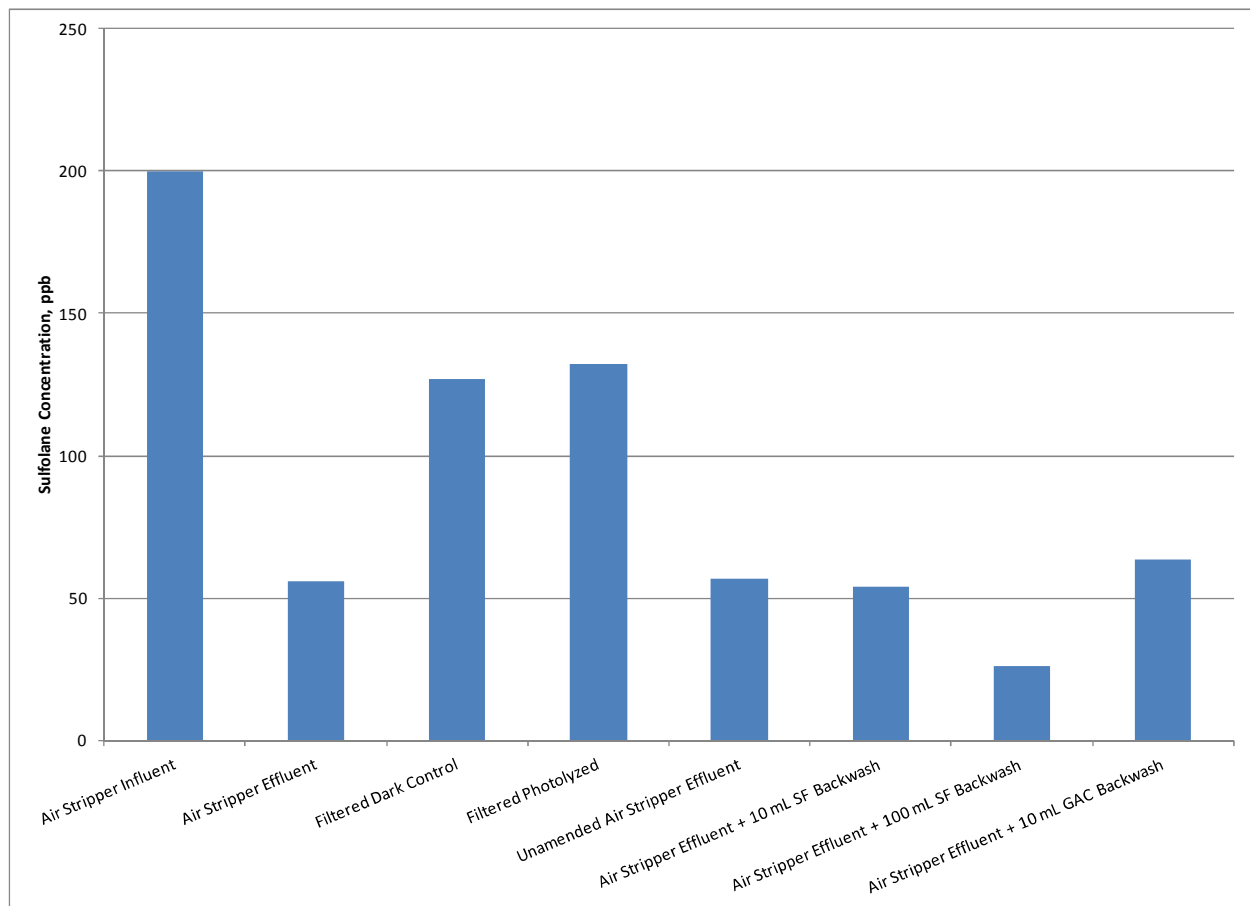**c:**   Brian Angerman, Brian Sillanpaa, Gary Remple

Figure 1: Sulfolane Results for Test 1

Test 2

Test 2 was conducted onsite in August 2011. This test sought to impose factors (i.e. low dissolved oxygen and cold temperatures) that may limit the mechanism in situ relative to in the remediation system. Secondarily, the test sought to elucidate the relationship between iron/manganese redox conditions and sulfolane removal. The test was conducted in a series of sealed glass bottles, prepared using anoxic groundwater from recovery well R35-R, sand filter backwash solids (in the same proportion applied in Test 1), and varying air: water ratios within the bottles (0:1 to 1:1). Replicate treatments were incubated for 4 hours at three different temperatures (2 degrees C, 4 degrees C, 8 degrees C). Treatments in which the amounts of reduced iron and/or reduced manganese were increased via addition of chloride salts were

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also included. Controls representing iron/manganese oxidation in the absence of backwash were also included. As it was learned from Test 1 that filtration of the samples could quench an otherwise ongoing reaction, samples were filtered upon completion of incubation prior to shipping to the lab. The treatments applied are summarized below:

Table 2: Summary of treatments for Test 2

Jar ID	Air:Water Ratio	Temperature	Backwash	$FeCl_2$, mg/L	$MnCl_2$, mg/L
1	0:1	2	Yes	0	0
2	0.5:1	2	Yes	0	0
3	1:1	2	Yes	0	0
4	1:1	2	No	0	0
5	0:1	4	Yes	0	0
6	0.5:1	4	Yes	0	0
7	1:1	4	Yes	0	0
8	1:1	4	No	0	0
9	0:1	8	Yes	0	0
10	0.5:1	8	Yes	0	0
11	1:1	8	Yes	0	0
12	1:1	8	No	0	0
13	0:1	2	Yes	2	2

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| 14 | 0:1 | 2 | Yes | 2 | 0 |
| 15 | 0:1 | 2 | Yes | 0 | 2 |

The results of Test 2 are summarized in Figure 2. It can be seen from Figure 2 that decreasing the reaction temperature did not affect the degree of sulfolane removal observed. It can also be seen that the degree of sulfolane removal observed was less than reported in Test 1, further suggesting an ongoing reaction in the unfiltered Test 1 samples in transit to the laboratory. The test results also confirmed the role of backwash solids in the reaction, as controls without backwash solids exhibited less sulfolane removal than their backwash-amended counterparts.

Interestingly, inclusion of greater amounts of oxygen (via higher air:water ratios) increased the amount of sulfolane removal observed in the 2 degree C treatments, but decreased sulfolane removal in the warmer treatments. Also of interest is the observation of the greatest degree of sulfolane removal in the anoxic treatments that were amended with ferrous iron, but not manganese.

Figure 3 summarizes observed sulfolane concentrations relative to the concentrations of dissolved (i.e. reduced) iron and manganese at the end of the incubation period. It can be seen from Figure 3 that, while reduced iron and sulfolane concentrations declined in the treatments, reduced manganese concentrations increased. The exceptions to this trend were those treatments in which reduced manganese was added. In these treatments, sulfolane concentrations did not exhibit the same inverse relationship to reduced manganese.

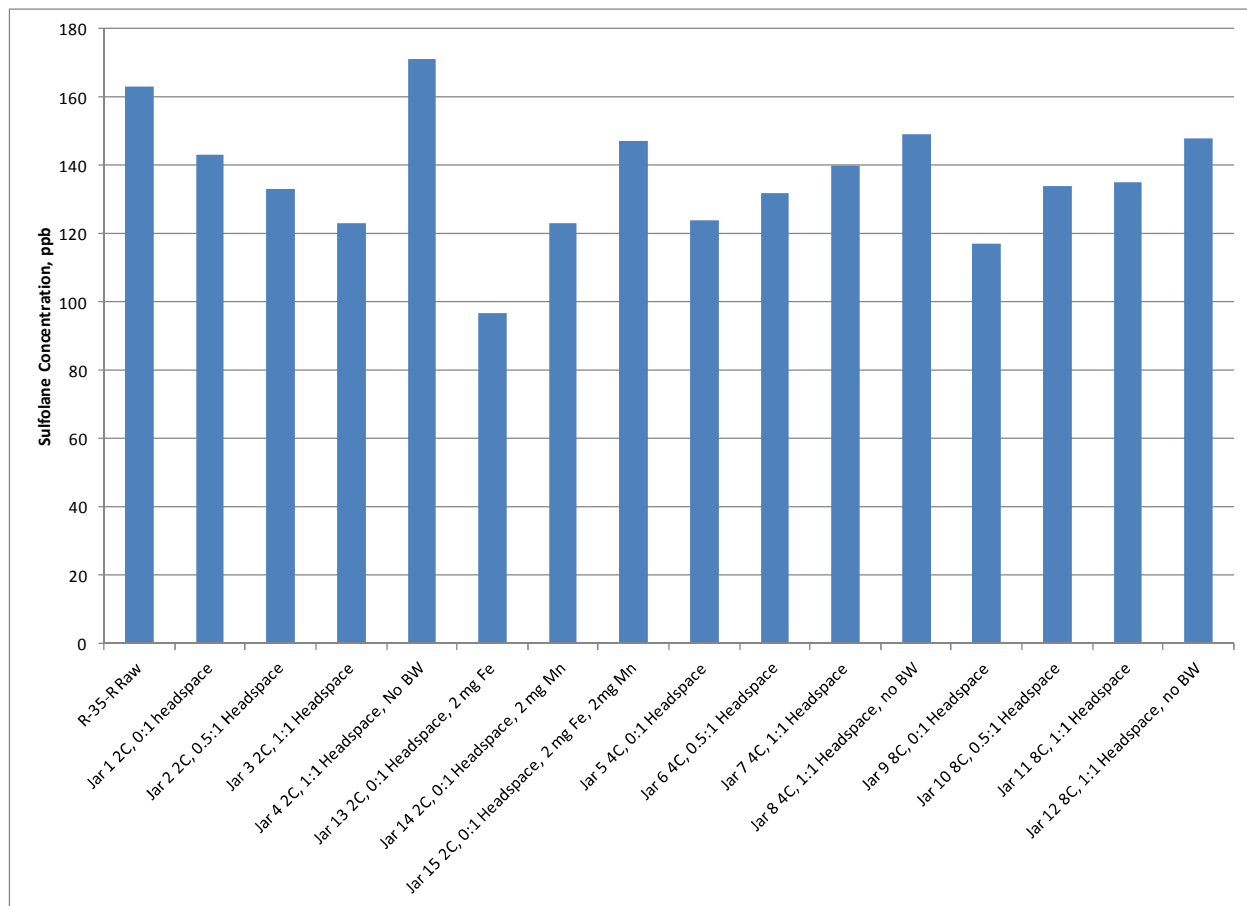| **To:**	Loren Garner
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Figure 2: Test 2 Sulfolane Results

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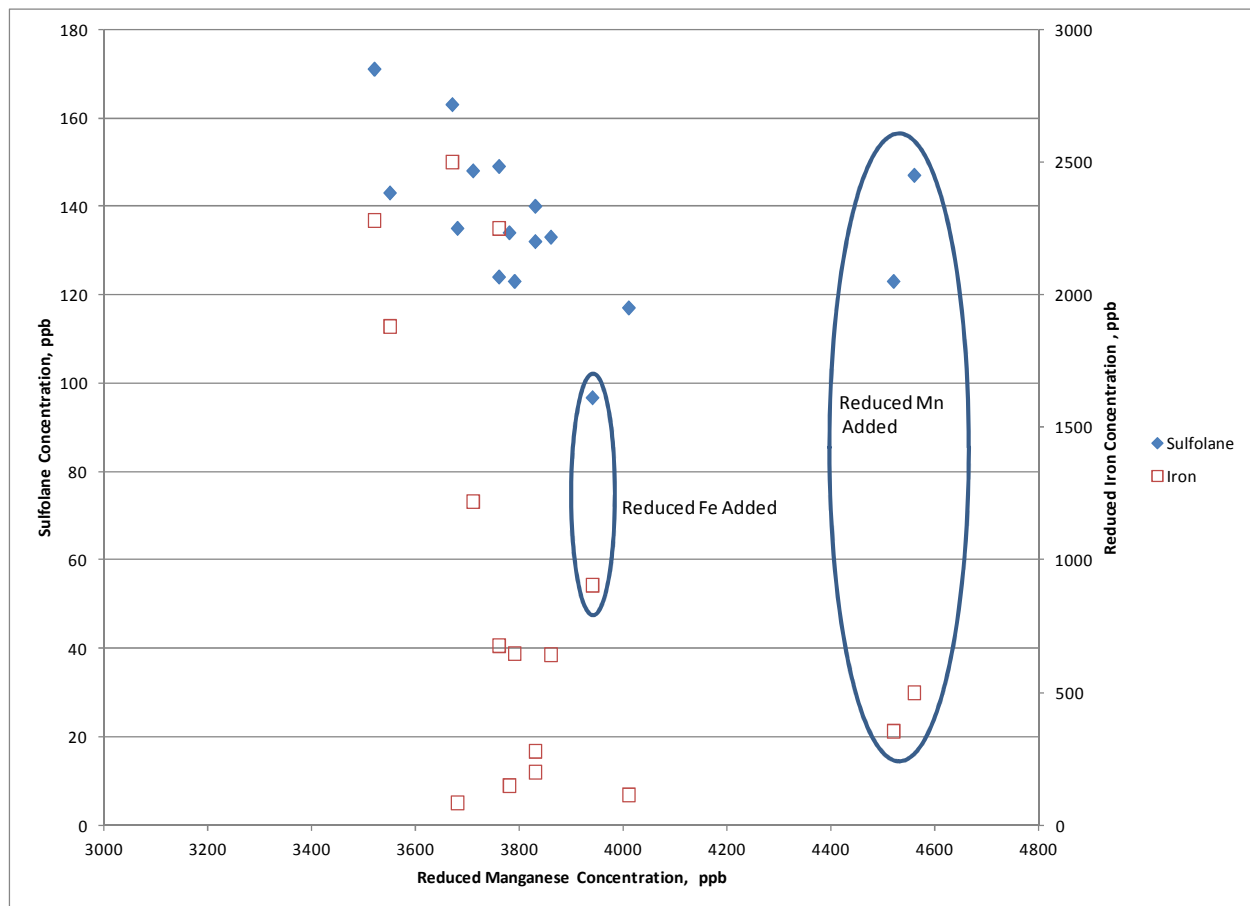**c:** Brian Angerman, Brian Sillanpaa, Gary Remple

Figure 3: Sulfolane Concentrations Relative to Reduced Iron and Manganese, Test 2

The hypothesis formulated based on the results of Test 2 was that sulfolane removal may occur via biological or abiotic mechanism(s) in conjunction with the coupled oxidation of iron and reduction of manganese, catalyzed by the backwash solids.

Test 3

Test 3 was conducted in December 2011 at Barr's Minneapolis laboratory. This test sought to gain insight into the abiotic or biological nature of the reaction by comparing results for laboratory-synthesized iron/manganese oxides with results for sand filter backwash solids, as well as the inclusion of nitrogen and phosphorus nutrients in the reaction. Further, the test sought to clarify the role of dissolved oxygen in

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the reaction, as Test 2 had yielded some conflicting results in that regard. All treatments were constructed using synthetic groundwater, thus limiting background noise and potentially facilitating the identification of reaction intermediates and daughter products for those treatments exhibiting significant sulfolane removal. As the hypothesized reaction mechanism(s) included abiotic reactions involving backwash solids, treatments in which the solution pH was adjusted to 6 were included to evaluate potential effects on the mechanism(s) due to changes in iron solids surface chemistry with pH.

The treatments applied are summarized in Table 3.

Preparation of the mixed oxides

Mixed iron/manganese oxides were prepared in 500-mL batches by adding the required dosages of ferrous and manganous chloride to distilled water, adjusting the pH to 7 with sodium hydroxide, and aerating with compressed air for 24 hours. Table 4 lists the required dosages of manganous and ferrous chloride. The dosages were selected to mimic the total metals concentration in the sand filter backwash, but also vary the relative amounts of iron and manganese in the oxides in within ranges observed in site groundwater.

Table 4: Summary of dosages for synthesis of iron/manganese oxide slurries

Target Fe:Mn Ratio in Oxide (wt:wt)	FeCl2 Dose, mg/L	MnCl2 Dose, mg/L
4:1	400	100
2:1	333	167
1:1	250	250
0.5:1	100	400

Preparation of synthetic groundwater

Synthetic groundwater was prepared in a single 15-L batch. The required dosages of calcium carbonate and magnesium sulfate (Listed in Table 5) were added to distilled water and mixed until dissolved. The solution were sparged with 5% CO2/balance N2 gas for 3 hours to deoxygenate the water.

Table 5: Summary of dosages for synthetic groundwater constituents

CaCO3, mg/L	MgSO4, mg/L
180	50

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Following sparging, a 5-liter aliquot of synthetic groundwater was removed and the pH adjusted to 6 using sulfuric acid. This aliquot was capped and reserved for construction of those reactors with pH 6.

Assembly of the batch reactors

1000-mL serum bottles were used to construct the anaerobic reactors, while 1000-mL beakers were used to construct the aerobic reactors. Batch reactors were assembled by combining 900 mL of synthetic groundwater with 100 mL of either mixed oxide slurry or backwash. In the case of reactors number 22-24, no solids were added, and these reactors contained 1000 mL of synthetic groundwater as described in Table 3. Those reactors receiving nutrients were amended via addition of the appropriate volume of nutrient stock solution. Those reactors receiving ferric/manganic chloride were amended with the appropriate dose of each. Each reactor was then spiked with 300 ppb of sulfolane (reagent-grade aqueous stock solution obtained from Acros Organics). The anaerobic reactors were filled and capped such that there was zero headspace, while aerated reactors were open to the atmosphere.

Reaction

All reactions were carried out at 4 degrees C to mimic typical shallow groundwater temperatures. The reaction time was 8 hours. Following the 8-hour reaction time, the contents of the reactors were immediately pressure filtered through a 0.45-micron filter and sampled for sulfolane, dissolved iron, and dissolved manganese. As part of the sulfolane analysis, the full chromatogram was examined for potential daughter products. The filtered solids were retained and stored at 4 degrees C for later extraction and analysis for sulfolane/daughter products.

Results

Sulfolane results are summarized in Figure 4. As shown in Figure 4, the greatest degree of sulfolane removal was observed in the aerated backwash solids. Lesser degrees of sulfolane removal were observed in the anaerobic backwash solids, as well as the aerated Fe(II)/Mn(II) treatment that contained no backwash solids. In those reactors exhibiting sulfolane removal, the pH 6 treatments exhibited greater sulfolane removal than their pH 8 counterparts. The anaerobic reactors containing laboratory-synthesized oxides did not exhibit significant sulfolane removal. The inclusion of nitrogen and phosphorus nutrients

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in the aerated backwash treatments resulted in slightly greater sulfolane removal relative to their counterparts without nutrients. Nutrients did not appear to affect sulfolane removal in the anaerobic treatments.
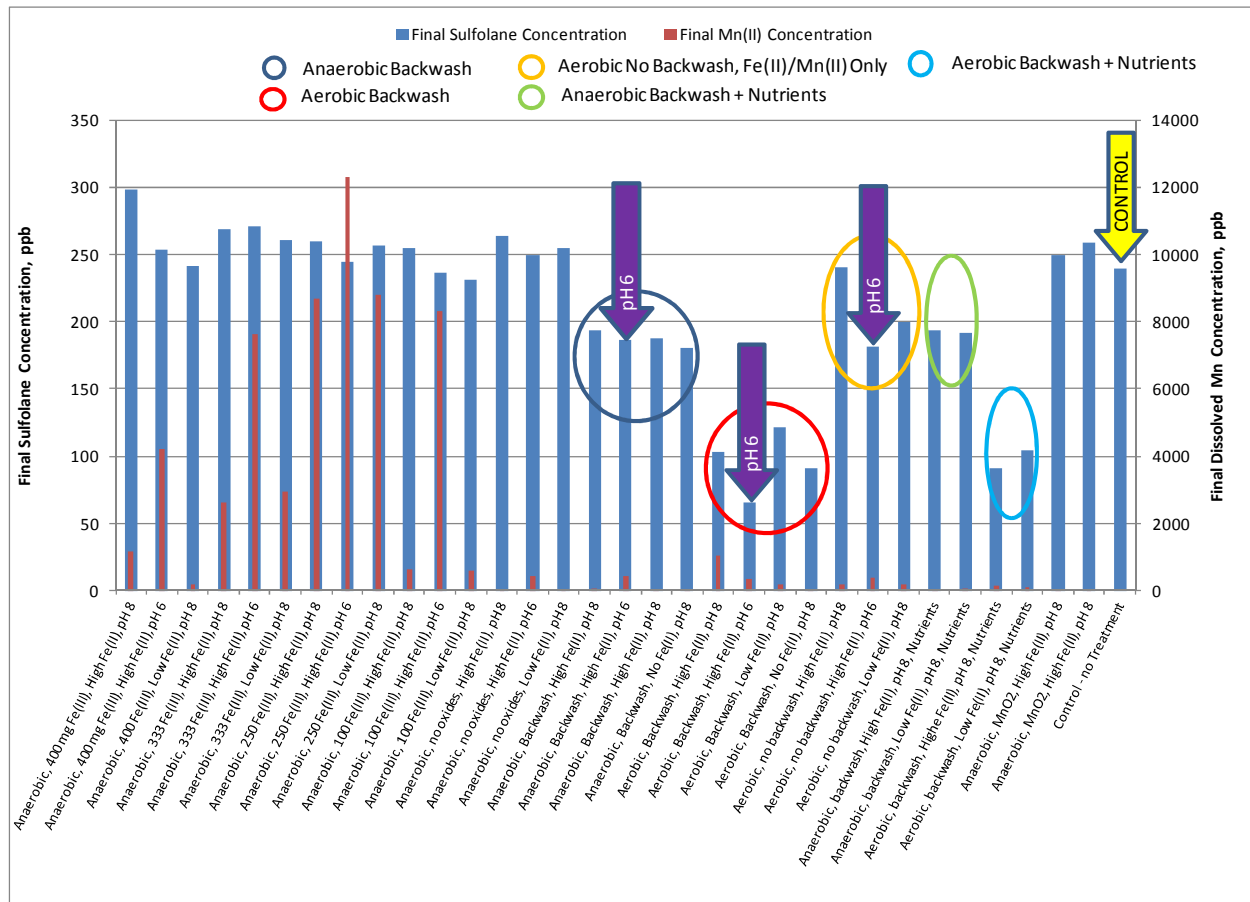

Figure 4: Sulfolane and Manganese Results, Test 3

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Table 3: Summary of experimental conditions for Test 3

Jar ID	Oxide Slurry Dose, mL							Aqueous Conditions		Aeration	Nutrients, µg/L	
	4:1 $FeCl_2$:$MnCl_2$	2:1 $FeCl_2$:$MnCl_2$	1:1 $FeCl_2$:$MnCl_2$	0.5:1 $FeCl_2$:$MnCl_2$	0.5:1 $FeCl_3$:MnO_2	MnO_2 Only	SF Backwash	$FeCl_2$:$MnCl_2$ (mg/L:mg/L)	pH		NH_4NO_3	KH_2PO_4/ K_2HPO_4 (1:1)
1	100							1:0.2	8	No	0	0
2	100							1:0.2	6	No	0	0
3	100							0.2:0.2	8	No	0	0
4		100						1:0.2	8	No	0	0
5		100						1:0.2	6	No	0	0
6		100						0.2:0.2	8	No	0	0
7			100					1:0.2	8	No	0	0
8			100					1:0.2	6	No	0	0
9			100					0.2:0.2	8	No	0	0
10				100				1:0.2	8	No	0	0
11				100				1:0.2	6	No	0	0
12				100				0.2:0.2	8	No	0	0
13					100			1:0.2	8	No	0	0
14					100			1:0.2	6	No	0	0
15					100			0.2:0.2	8	No	0	0
16							100	1:0.2	8	No	0	0
17							100	1:0.2	6	No	0	0
18							100	0.2:0.2	8	No	0	0
19							100	None	8	No	0	0
20							100	1:0.2	8	Yes	0	0
21							100	1:0.2	6	Yes	0	0
22							100	0.2:0.2	8	Yes	0	0
23							100	None	8	Yes	0	0
24								1:0.2	8	Yes	0	0
25								1:0.2	6	Yes	0	0
26								0.2:0.2	8	Yes	0	0
27							100	1:0.2	8	No	10	0.2/0.2

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Table 3: Summary of experimental conditions for Test 3

| Jar ID | Oxide Slurry Dose, mL | | | | | | | Aqueous Conditions | | | Nutrients, µg/L | |
	4:1 FeCl2:MnCl2	2:1 FeCl2:MnCl2	1:1 FeCl2:MnCl2	0.5:1 FeCl2:MnCl2	0.5:1 FeCl3:MnO2	MnO2 Only	SF Backwash	FeCl2:MnCl2 (mg/L:mg/L)	pH	Aeration	NH4NO3	KH2PO4/K2HPO4 (1:1)
28							100	0.2:0.2	8	No	10	0.2/0.2
29							100	1:0.2	8	Yes	10	0.2/0.2
30							100	0.2:0.2	8	Yes	10	0.2/0.2
31						100		1:0	8	No	0	0
32						100		None	8	No	0	0

Several of the treatments exhibiting sulfolane removal, as well as the sulfolane-spiked control, were selected for post-processing of the chromatography and mass spectroscopy data to look for reaction intermediates and daughter products. Post-processing included tentative identification of observed compounds and preliminary estimation of their concentrations. The treatments selected for post-processing were:

- Jar 33 (the sulfolane-spiked control)
- Jar 17 (anaerobic backwash solids, pH 6)
- Jar 21 (aerobic backwash solids, pH 6)
- Jar 25 (aerobic Fe(II)/Mn(II), no backwash solids, pH 6)

The chromatograms were examined for those peaks appearing in the treatments that were not present in the sulfolane-spiked control. For those peaks whose elution times differed slightly, the mass spectra were compared to determine if the peaks were likely from the same compound. Table 6 summarizes the interpretation of the gas chromatography and mass spectroscopy data.

Table 6: Summary of interpretation of gas chromatography and mass spectroscopy data, Test 3.

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	Jar ID				
Elution Time, min	17 Anaerobic BW	21 Aerobic BW	25 Aerobic, no BW	33 Control	Comments
6.9	x				Present in Anaerobic Treatment
7.04		x	x		Present in Aerobic Treatments
9.095	x	x	x	x	
10.09	x	x	x	x	
11.66	x	x	x	x	
11.811				x	Same Spectra
12.147	x				
12.62		x	x		Present in Aerobic Treatments
12.733				x	Same Spectra
12.859				x	
13.03	x	x	x	x	Same Spectra
13.046				x	
13.164	x	x			Same Spectra
13.227			x		
13.267				x	
13.477				x	Same Spectra
13.622				x	
13.816				x	
13.995	x	x	x		Same Spectra
14.024				x	
14.132				x	Same Spectra
14.476				x	

Compounds identified in the treatments, but not in the control included:

- A compound with an elution time of 6.9 minutes and a characteristic ion with m/z = 88 observed in the anaerobic treatment
- A compound with an elution time of 7.06 minutes and a characteristic ion with m/z = 137 observed in both aerobic treatments
- A compound with an elution time of 12.62 and a characteristic ion with m/z = 244 observed in both aerobic treatments

The compounds identified above were evaluated relative to sulfolane, which has an elution time of 6.5 minutes and a characteristic ion with m/z = 120.

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The compound detected in the anaerobic reactor with an elution time of 6.9 minutes and a characteristic ion with m/z = 88 would be consistent with sulfolane without the oxygen atoms. Such a compound, thiolane, has been detected in anaerobic settings with sulfolane contamination, as described in the literature review.

The compound detected in the aerobic treatments with an elution time of 7.04 minutes and a characteristic ion with m/z=137 would be consistent with sulfolane to which a hydroxyl group had been added. Such a compound, hydroxybutane sulfinic acid, has been theorized as an intermediate in aerobic sulfolane degradation in the literature.

The compound detected in the aerobic treatments with an elution time of 12.62 minutes and a characteristic ion with m/z = 240 would be consistent with dimerized sulfolane. Such a dimer has been described in the literature as an observed product of sulfolane cleavage via a metal catalyst.

Table 7 summarizes a rough mass balance conducted using the estimated change in sulfolane concentration, along with the estimated concentrations of the detected daughter products. As shown in the table, the mass recovery was reasonably good for the anaerobic and Fe(II)/Mn(II) aerated reactors. Mass recovery was substantially lower in the aerated backwash reactor.

Table 7: Rough mass balance on sulfolane and daughter products, Test 3

Jar ID	Initial Sulfolane, ppb (Estimated from control)	Final Sulfolane, ppb	Estimated Thiolane, ppb	Estimated hydroxybutene sulfonic acid, ppb	Estimated Sulfolane Dimer, ppb	Mass Recovered
17	239	186	24.8	0	0	88%
21	239	65.2	0	32.6	43.6	59%

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25	239	181	0	38.9	25.6	103%

Finally, the solids filtered from Jars 17, 21, and 25 were extracted in methylene chloride, and the extracts analyzed for sulfolane, as well as tentatively identified organic compounds. While the mass of solids on the filters was insufficient to allow results to be quantitatively normalized to dry solid weight, the compounds extracted from the solids can give insight into the reaction mechanisms responsible for the observed disappearance of sulfolane. A clean filter was extracted in methlyene chloride to provide a blank for comparison of results.

No sulfolane was detected in the extract from any of the reactors. No apparent sulfolane intermediates were detected in the solids from the anaerobic reactor – all the detected compounds were present in either the clean filter blank or the sulfolane-spiked control. A compound with a retention time of 13.924 minutes and a characteristic ion with an $m/z = 167$ was detected in significant amounts in the solids from the aerobic reactors. This m/z would be consistent with the larger product of sulfolane dimer cleavage as shown below:
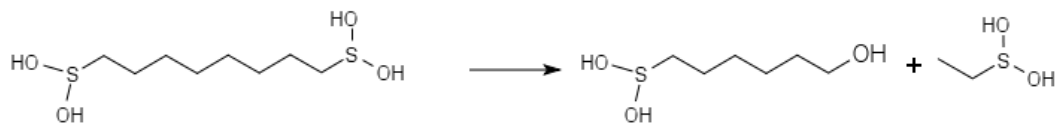
Test 3 Conclusions

The fact that sulfolane removal was observed under aerobic and anaerobic conditions suggests that sulfolane removal may occur under either condition. Sulfolane removal under aerobic conditions was more complete, however, suggesting that the aerobic pathway may be more rapid.

The observation of sulfolane removal upon aeration of an Fe(II)/Mn(II) solution in the absence of backwash solids suggests a potential abiotic removal mechanism. The observation of limited improvement of sulfolane removal upon addition of nutrients further suggests that an abiotic reaction may

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be important. The improvement of sulfolane removal at pH 6, particularly in the aerobic reactors, further supports the involvement of an abiotic reaction mechanism in sulfolane removal.

Two of the daughter products observed in the reactors matched compounds reported in the biodegradation literature – thiolane having been observed in anaerobic settings, and hydroxybutene sulfinic acid having been theorized as an intermediate in aerobic sulfolane biodegradation. The sulfolane dimer observed in the aerobic reactors is consistent with the product of abiotic metal-catalyzed sulfolane dimerization described in the chemical engineering literature.

The recovery of all the lost sulfolane mass as measured daughter products in the aerated Fe(II)/Mn(II) reactor, but not in the aerated backwash reactor, suggests that the measured daughter products may have been the result of an abiotic reaction. Microbes present in the backwash solids may have degraded those products to simpler compounds that were not detectable via gas chromatography, resulting in a lower mass recovery in the reactor with aerated backwash solids.

The absence of sulfolane in the extract from the reactor solids confirmed that the sulfolane was not adsorbed to the solids. Additionally, detection of a fragment of sulfolane dimer in the filtered solids from the aerobic reactors further supports the notion that the sulfolane degradation process involves cleavage of the cyclobutene ring at the iron oxide surface.

Proposed Sulfolane Degradation Pathways

The following sections describe proposed sulfolane degradation pathways based on synthesis of the published literature and the findings from bench testing conducted. While these pathways were largely inferred from sulfolane removal across the air strippers, gallery pond, and sand filter, they also may have applicability to in-situ remedial techniques, such as air sparging and monitored natural attenuation.

Proposed Aerobic Pathways

Figure 5 illustrates the proposed aerobic pathways for sulfolane degradation. The steps illustrated in the figure are detailed below.

Step 1 – Oxidation of ferrous iron/reduction and cleavage of sulfolane cyclobutene ring

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Ferrous iron may be initially coordinated with aqueous sulfolane. Introduction of oxygen, along with a catalytic iron/manganese oxide surface may facilitate oxidation of the iron, along with transfer of two electrons to the sulfolane molecule. While technically an oxidative addition reaction, this is a special case in which the metal (iron) is oxidized and the ligand (sulfolane) is reduced.

The addition reaction results in cleavage of the cyclobutene ring at one of the S-C bonds. The cleaved carbon at the end of the chain now possesses two unpaired electrons (a radical). The reaction appears to be exothermic, thus may actually proceed more rapidly at lower temperatures-a notion that is supported by sulfolane removal observed during winter operation of the remediation system.

Step 2 – Interaction of the free radical

The radical generated from Step 1 above is short-lived in aqueous solution. Two possible interactions, resulting in quenching of the free radical, have been identified.

2a – Interaction of the radical with oxygen

The radical may interact with oxygen and water, resulting in the addition of a hydroxyl group to the end of the butene chain. The resulting molecule would be an alcohol, specifically, a hydroxybutene sulfinic acid. This molecule is an intermediate that has been hypothesized by researchers studying aerobic biodegradation of sulfolane (Greene et al., 2000). As previously described, a compound possessing an m/z identical to hydroxybutene sulfinic acid and an elution time longer than sulfolane was detected in aerobic bench treatments with and without backwash solids, but not in anaerobic treatments.

2b – Dimerization of the butene chains

The radicals on adjacent butene chains may interact with one another, resulting in a dimer of butene sulfinic acid. Such dimerization via metal catalysts is described in organic synthesis literature (Wellisch, et. al, 1964). Additionally, daughter products described in the deterioration of sulfolane in the sulfinol process loop include polymers and iron oxides. As previously described, a compound with an m/z identical to that of the dimer and an elution time significantly longer than sulfolane was detected in the aerobic treatments.

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3- Dissociation from the iron surface

The products formed at the iron surface may dissociate in a manner consistent with a solid-liquid distribution coefficient. This step may be affected by solution pH. The result is two potential products of differing length, as shown in Steps 3a and 3b.

4-Cleavage of the sulfonyl group

The sulfonyl groups may be cleaved from the ends of the products, resulting in sulfite and butanol, in the case of the hydroxybutene sulfinic acid (4a), or sulfur dioxide and octanol in the case of the dimer (4b). This cleavage may require catalysis via a microbial enzyme, such as a desulfinase.

5-Mineralization of remaining products

The remaining products may be mineralized via the following reactions

- Oxidation of sulfite and sulfur dioxide via oxygen to form sulfate
- Oxidation/assimilation of alcohols by heterotrophic bacteria
- Reduction of sulfite and sulfur dioxide to sulfide via sulfate reducing bacteria

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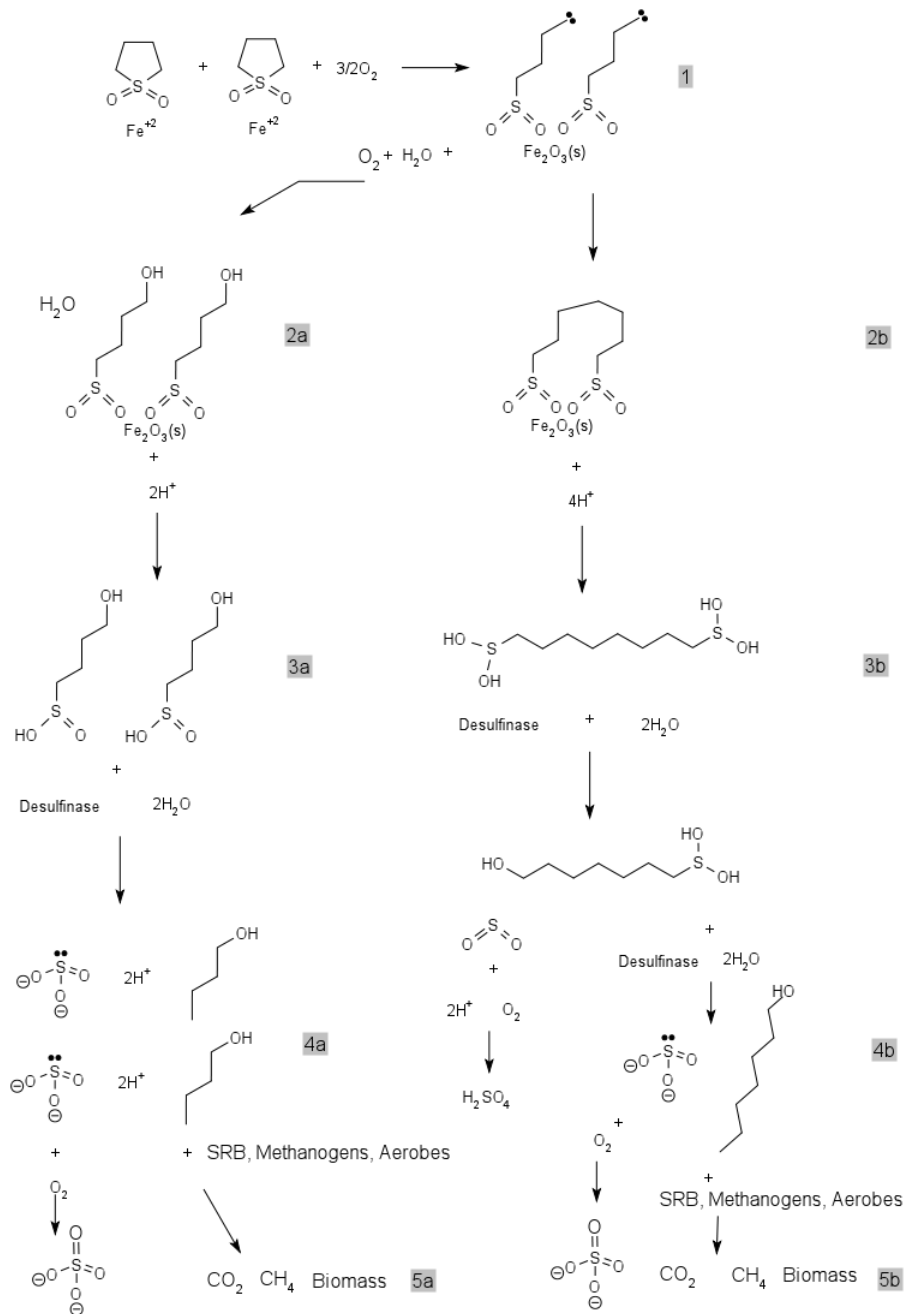**c:** Brian Angerman, Brian Sillanpaa, Gary Remple

Figure 5: Proposed Aerobic Pathways for sulfolane degradation

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Proposed Anaerobic Pathway

Figure 6 illustrates the proposed anaerobic pathway for sulfolane degradation. As in the aerobic pathways, this pathway involves the coupled reduction of sulfolane with iron oxidation. However, if insufficient dissolved oxygen is available to satisfy the requirement of the iron oxide, the oxygen may be removed from the sulfolane, resulting in thiolane. Thiolane is less polar than sulfolane, and thus would be more readily volatilized or adsorbed. The biodegradation of thiolane has not been well described in the literature.

Figure 6: Proposed anaerobic pathway for sufloane degradation

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Conclusions

The primary conclusion of this work is that sulfolane degradation may occur at the site under anaerobic or aerobic conditions in association with the oxidation of ferrous iron, which is generally plentiful in the site groundwater. Manganese oxides may also have a role, particularly under anaerobic conditions. Several pathways are possible, but all likely involve an initial abiotic reaction step involving sulfolane and iron, which renders the sulfolane molecule more susceptible to further biodegradation, adsorption, or volatilization.

The conditions that may be most conducive to sulfolane degradation therefore may be those that occur at the interface between reducing and oxidizing conditions, such as was imparted by the air strippers in the remediation system. Provided the reaction is not iron-limited, and the necessary catalytic oxide surfaces are available, increasing the dissolved oxygen concentration of the groundwater should drive degradation of sulfolane towards simpler end products (sulfate/sulfide, carbon dioxide/methane) via the hydroxybutene sulfinic acid intermediate.

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